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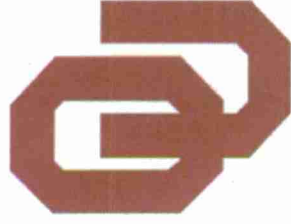
# Marine Corrosion in Fuel Systems

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Naval Research Laboratory, Stennis Space Center, MS



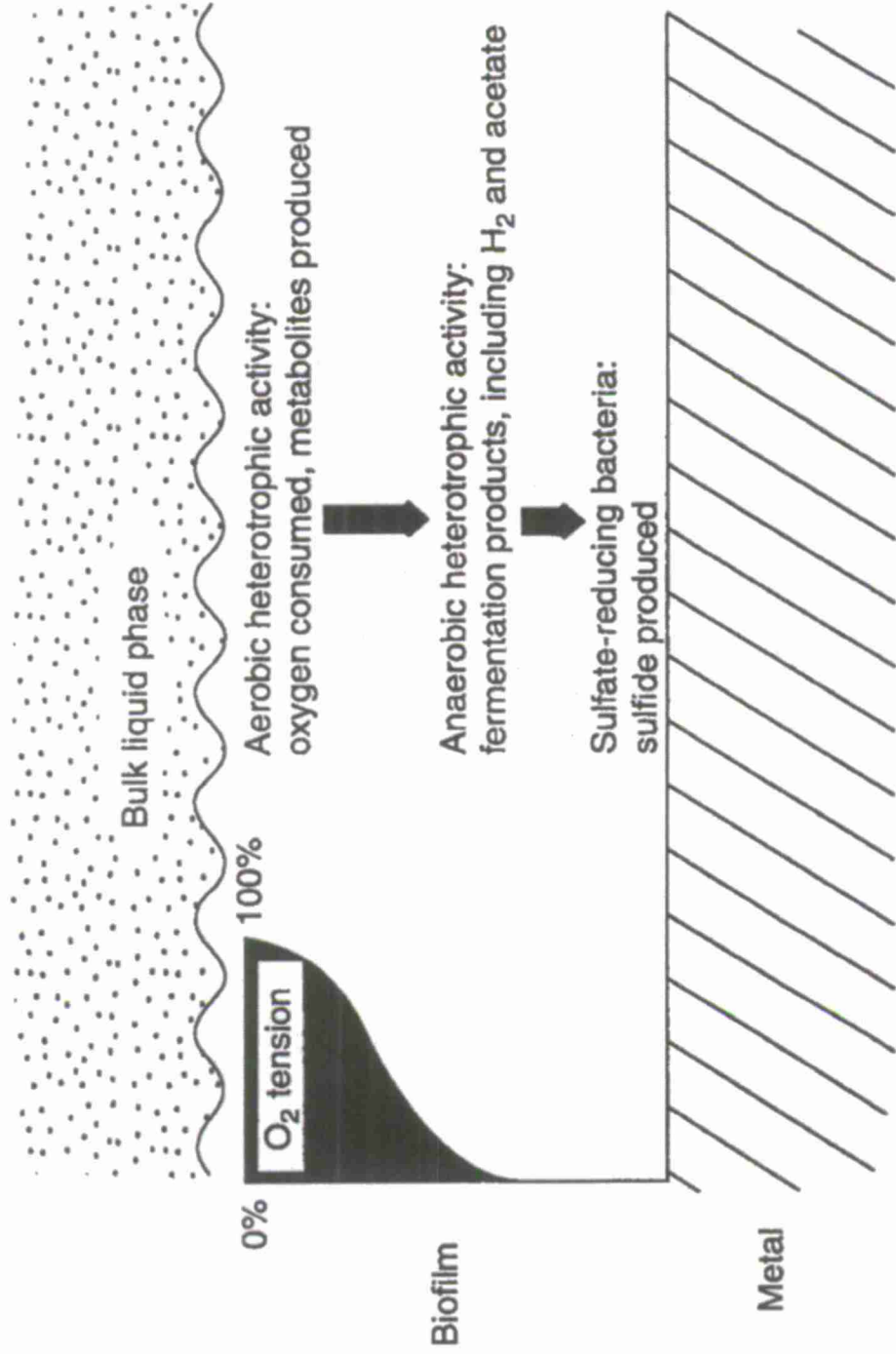
Deniz F. A Aktas, Kathleen E. Duncan, and Joseph M. Suflita  
University of Oklahoma, Norman, OK



2012/203011

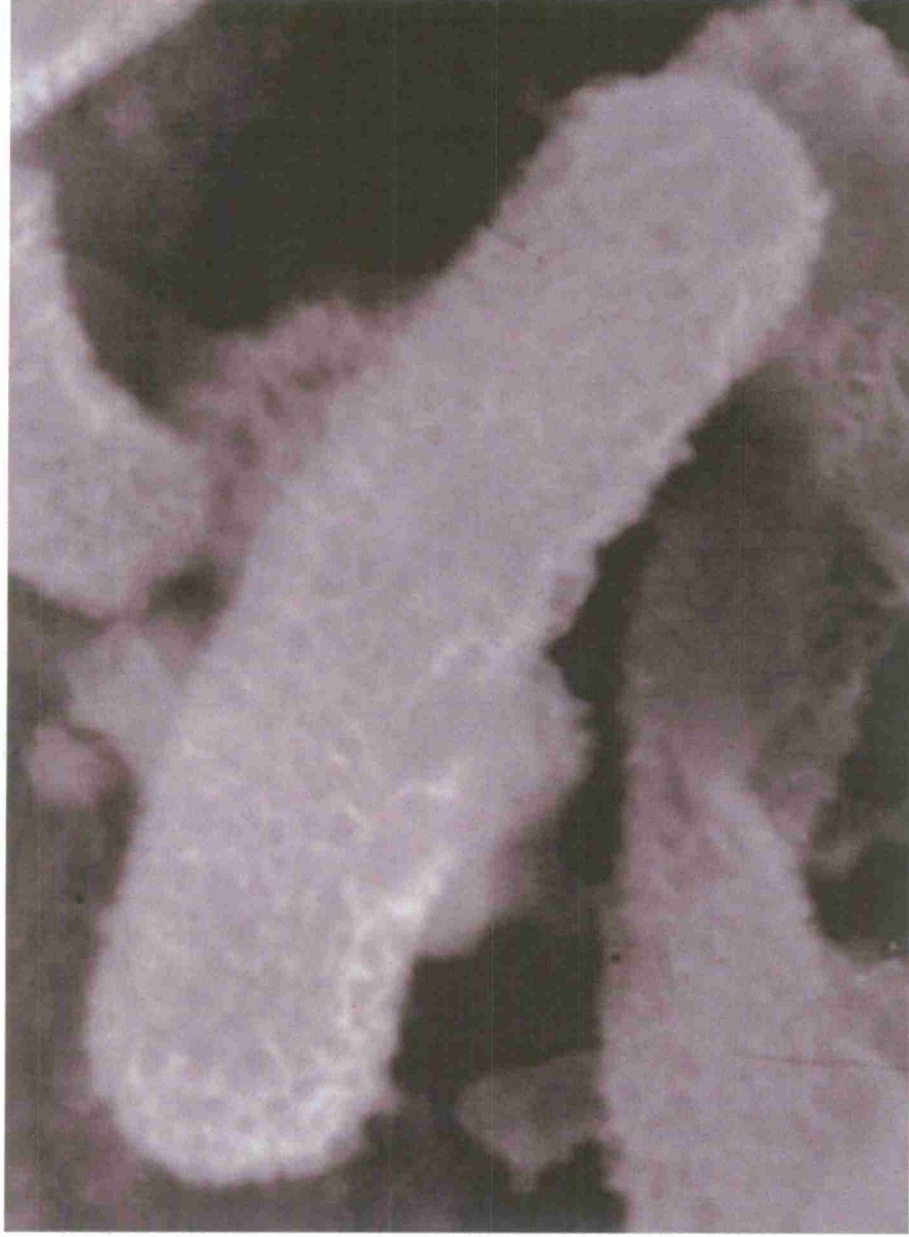
# Sulfide Derivitization

Seawater contains 2.0 grams  $L^{-1}$  sulfate

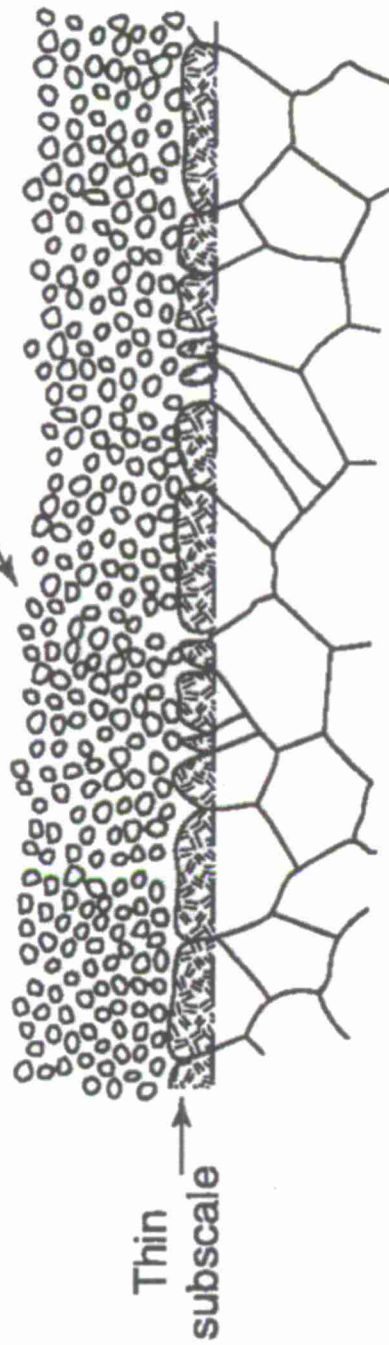


Hamilton (1985)

# Sulfate-Reducing Bacteria



Thick sulfide-rich scale

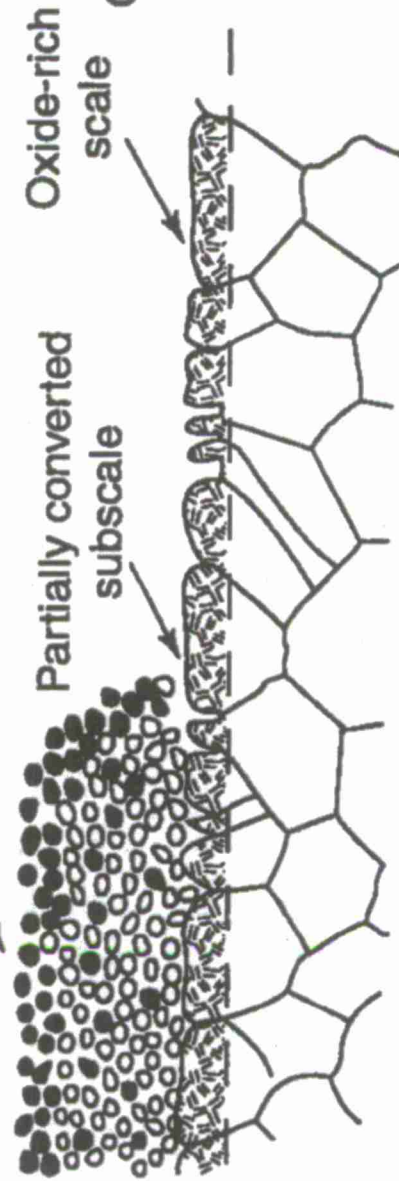


Corrosion product

Metal

(a)

Thick scale containing sulfide, partially converted sulfide, and oxide



Oxide-rich scale

Partially converted subscale

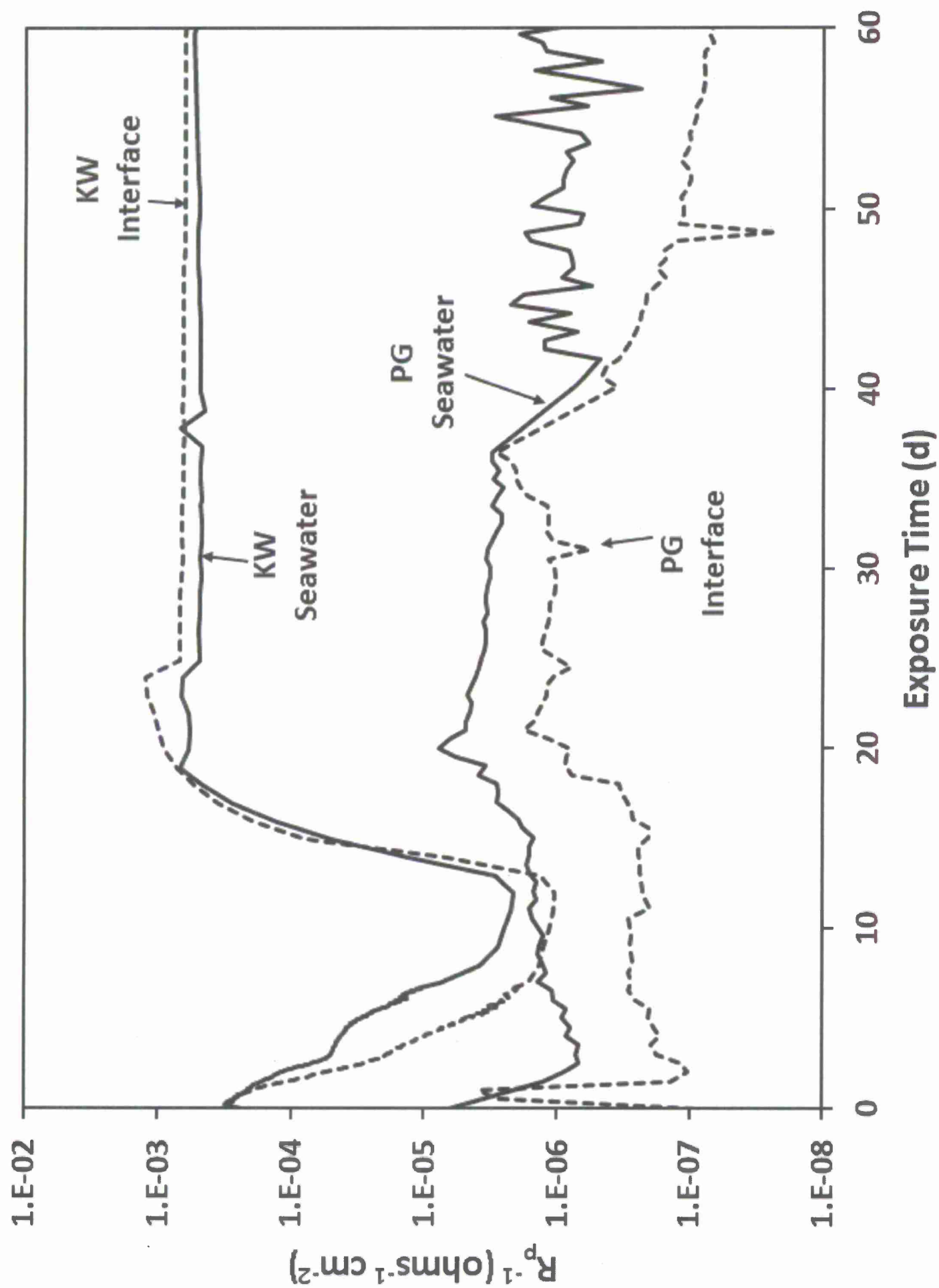
Corrosion product

Metal

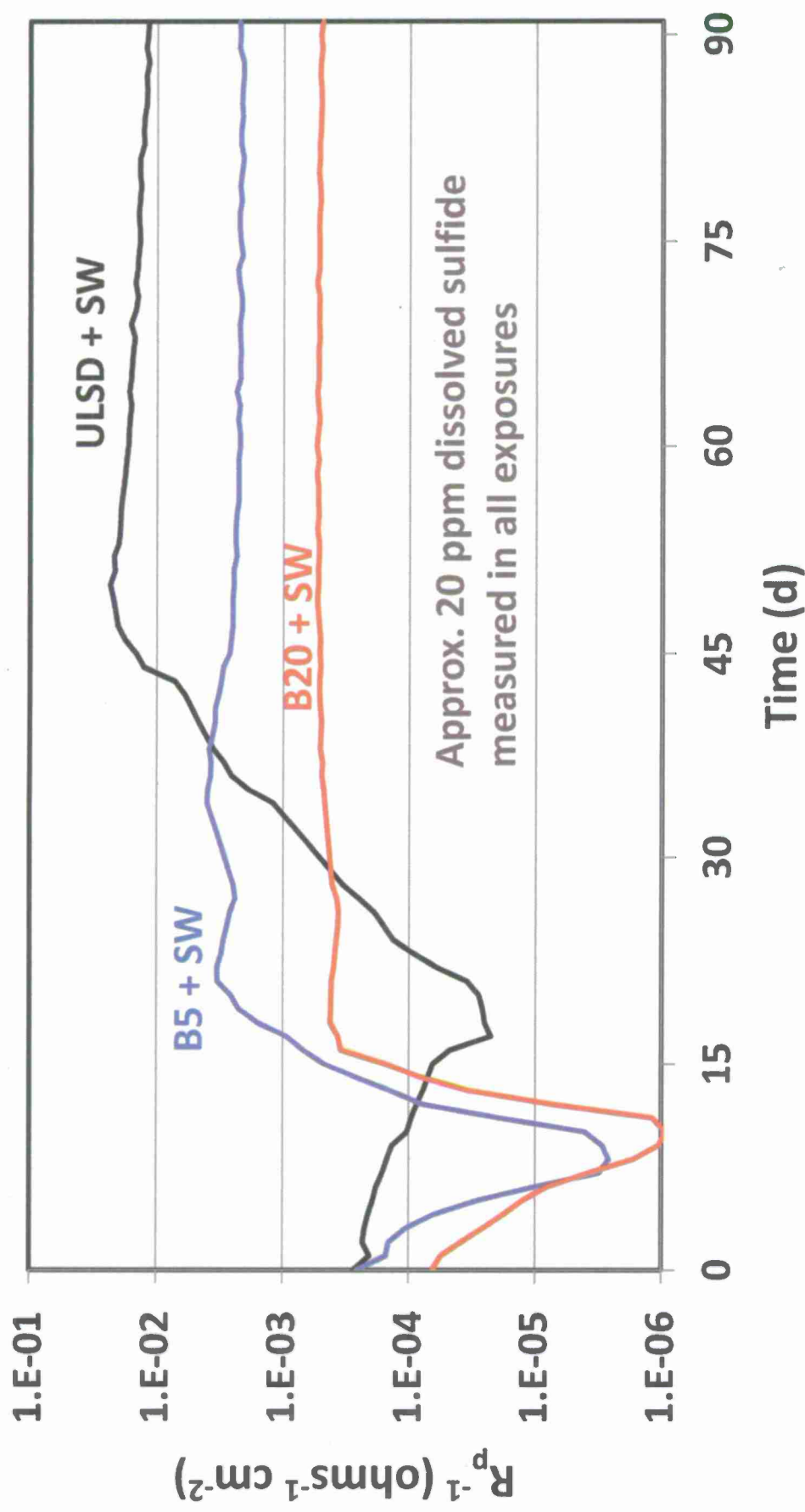
(b)

# Initial Chemistries

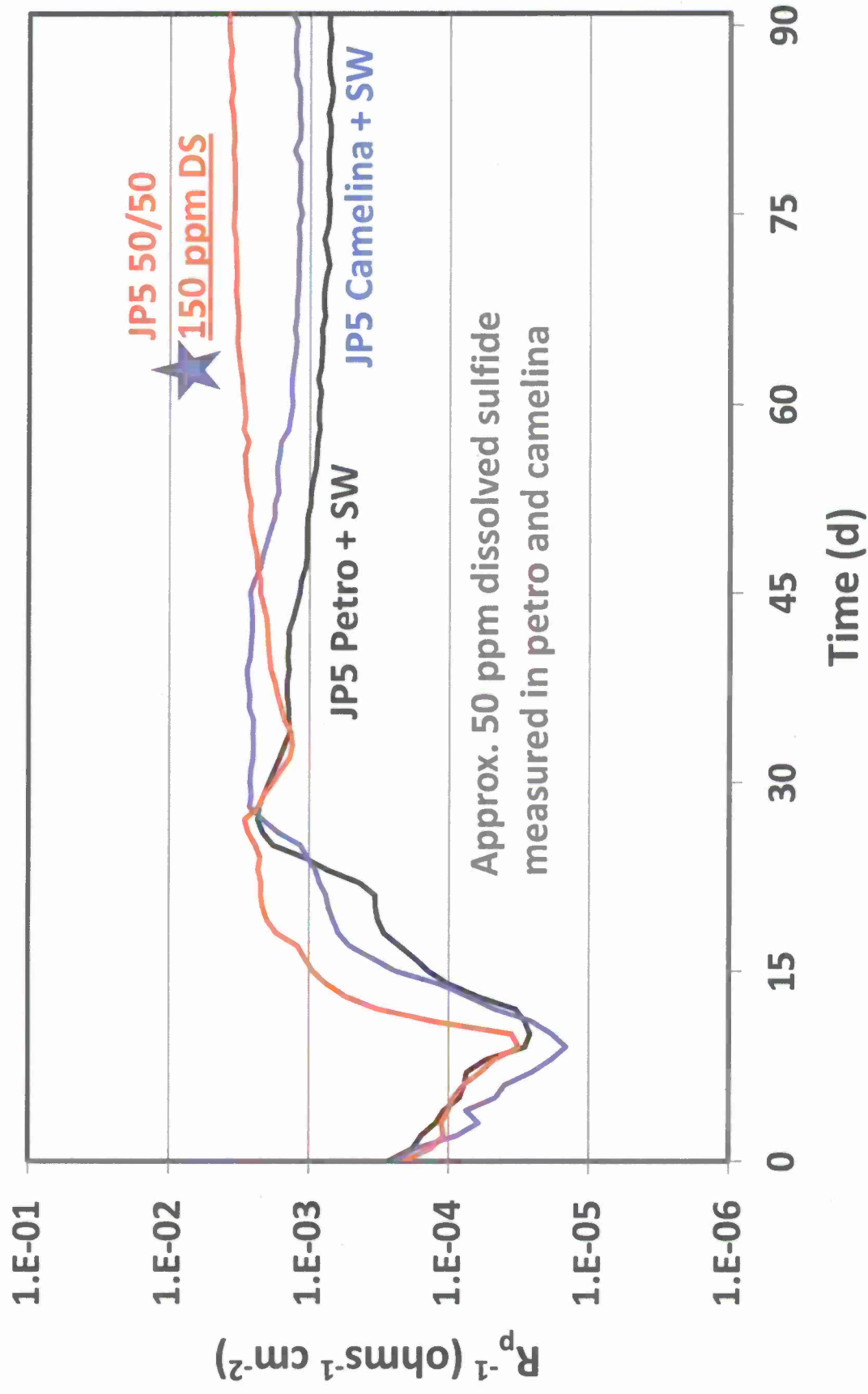
Seawaters	pH	Salinity (g/L)	Total Organic Carbon (mg/L)	Sulfate (mg/L)
Key West	7.82	38	1.79	3864
Persian Gulf	7.98	44	1.94	4696



# ULSD/FAME: Electrochemistry



# JP5: Electrochemistry



# Rates of sulphate reduction activity (SRA) in the seawater samples

Sample	SRA $\mu\text{mol S /L/day}$	SRA $\mu\text{mol S /L/day}$
	Persian Gulf Seawater PG	Key West Seawater KW
In situ (no additions)	$11.96 \pm 1.33$	$17.7 \pm 3.3$
Amended with lactate	$23.5 \pm 1.7$	115
Amended with crude oil*	$10.3 \pm 2.3$	$13.95 \pm 0.75$
Amended with crude oil and inoculated with strain Lake**	$155 \pm 6.7$	$264 \pm 40$
Sterile Control	$7.95 \pm 1.7$	$7.5 \pm 3.5$

\* sterile crude oil

\*\**Desulfoglaeba* strain Lake, an alkane-degrading sulphate-reducing bacterium

Table 2. Estimates of the number of different cell types based on quantitative PCR analyses

Estimates from qPCR	KW*	PG	KWBD	PGBD
Bacterial cells/mL	$2.75 \times 10^7$	$2.66 \times 10^7$	$4.97 \times 10^5$	$1.72 \times 10^5$
Dsr-bearing cells/mL**	3.17	BDL	BDL	BDL
Aps-bearing cells/mL***	BDL	BDL	BDL	BDL
Archaeal cells/mL	$3.05 \times 10^3$	$2.19 \times 10^3$	BDL	BDL
Mcr-bearing cells/mL****	$2.48 \times 10^3$	25	121	47.4

\*KW: Key West seawater; PG: Persian Gulf seawater; KWBD: FAME diesel incubated with KW seawater; PGBD: FAME diesel incubated with PG seawater.

\*\* Dsr-bearing cells: cells that contain a copy of the gene coding for dissimulatory (bi)sulphite reductase, e.g. SRB.

\*\*\* Aps-bearing cells: cells that contain a copy of the gene coding for adenosine-5'-phosphosulphate reductase, e.g. SRB.

\*\*\*\* Mcr-bearing cells: cells that contain a copy of the gene coding for subunit  $\alpha$  of methyl-S-CoM methylreductase, e.g. methanogens.

Table 3. Number of sequences classified as those of genera containing strains capable of degrading hydrocarbons

Genus	KW	PG	KWBD	PGBD
<i>Kordiimonas</i> ( $\alpha$ )*	14	0	9	0
<i>Gaetbulibacter</i> (Bact)**	4	1	0	0
<i>Marinobacter</i> ( $\gamma$ )***	0	1	1410	1918
<i>Alcanivorax</i> ( $\gamma$ )	4	9	0	0
<i>Cycloclasticus</i> ( $\gamma$ )	18	0	0	0
<i>Alteromonas</i> ( $\gamma$ )	4	10	2	5
<i>Pseudomonas</i> ( $\gamma$ )	1	1	0	0
<i>Shewanella</i> ( $\gamma$ )	0	2	0	0

\*  $\alpha$ : Alphaproteobacteria

\*\* Bact: Bacteroidetes

\*\*\*  $\gamma$ : Gammaproteobacteria

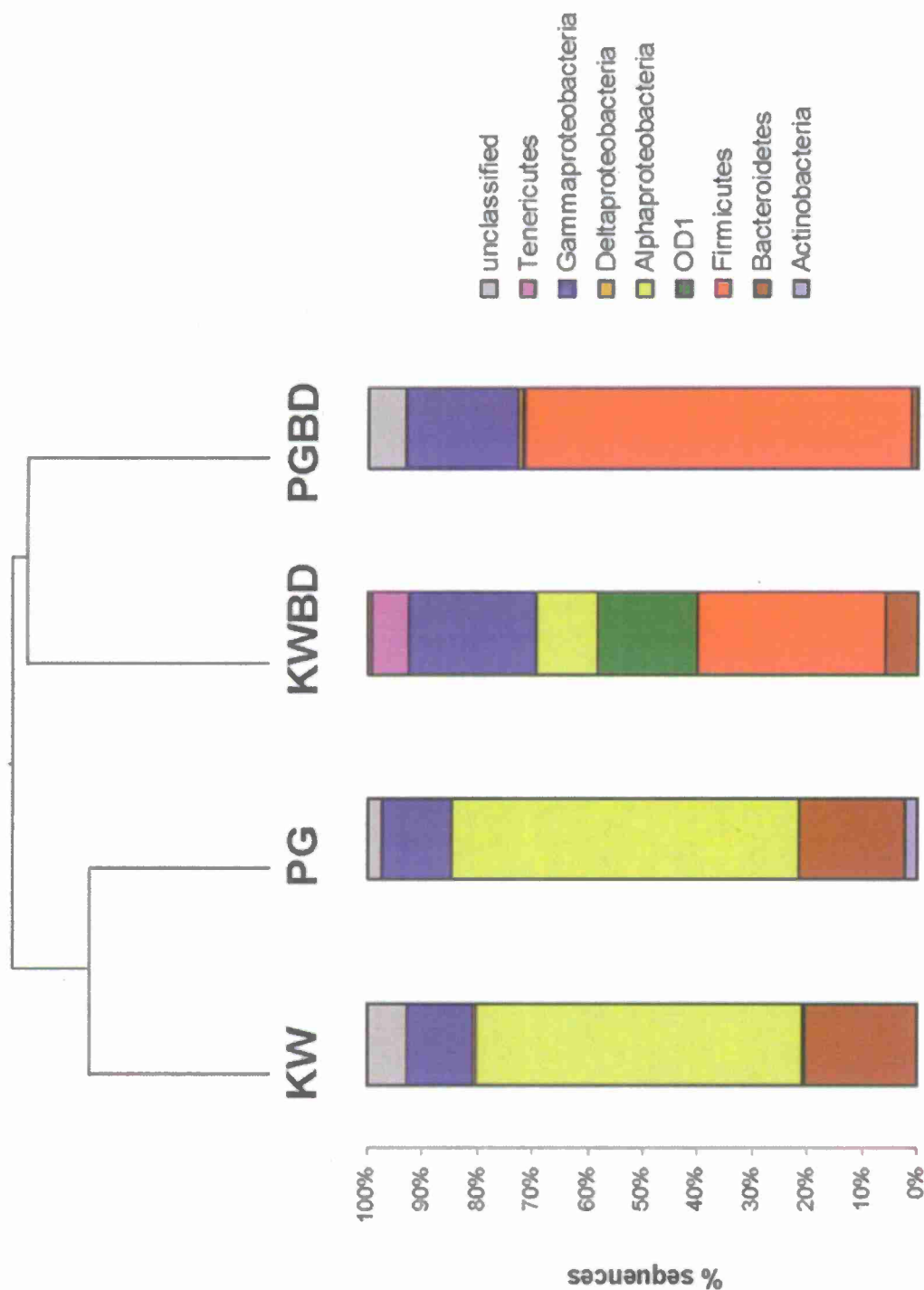
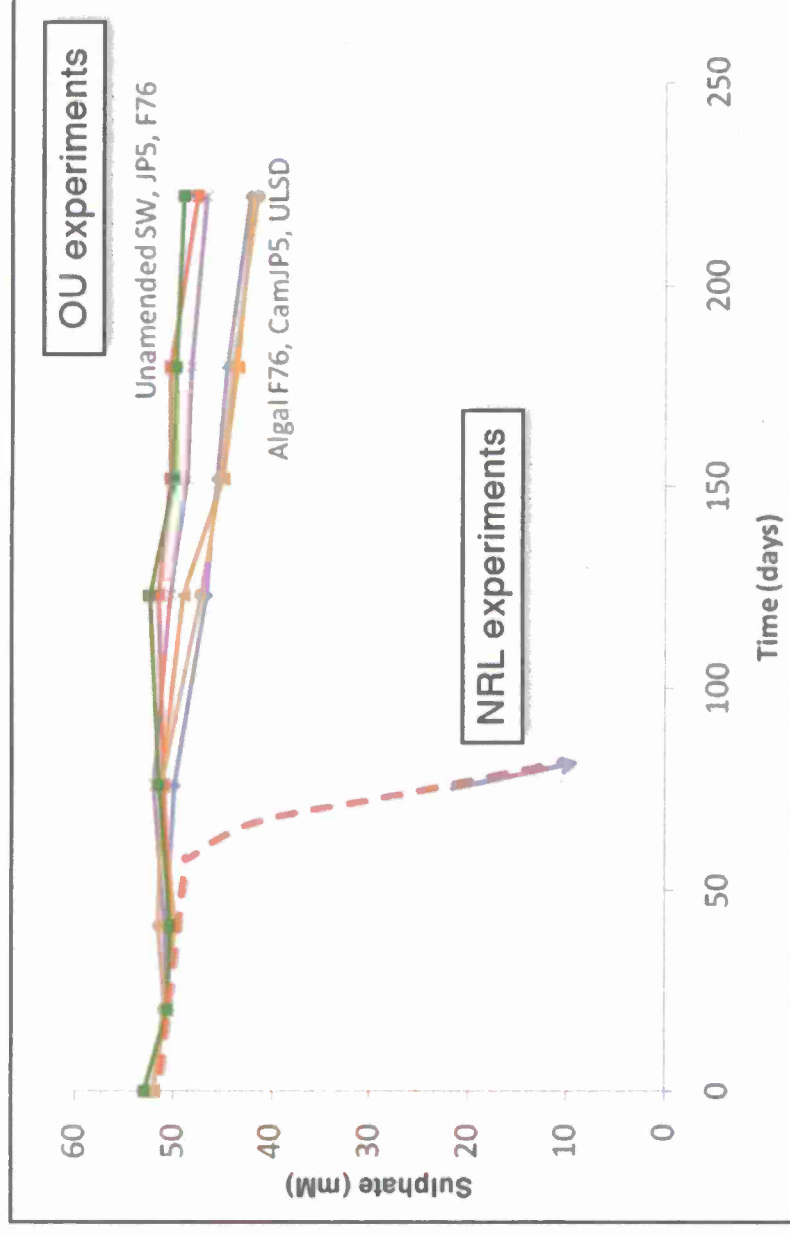


Figure 1. Analysis of bacterial 16S rRNA gene libraries created by pyrosequencing. Top. Dendrogram showing similarity among natural seawater samples (KW, PG) and FAME diesel/seawater incubations (KWBD, PGBD) based on a measurement of community structure ( $\theta_{YC}$ ) (Yue and Clayton 2005). Bottom: Relative abundances of sequences at the level of Phylum (Proteobacteria represented as Classes). Analyses were performed using the mothur software package (Schloss et al. 2009).

# Sulfate removal during anaerobic biodegradation of fuels



SW: seawater

JP5: jet petroleum

F76: petroleum diesel

algal F76: Algal derived diesel

Cam/JP5: camelina-derived jet fuel

# Initial Oxygen Conditions

**NRL**

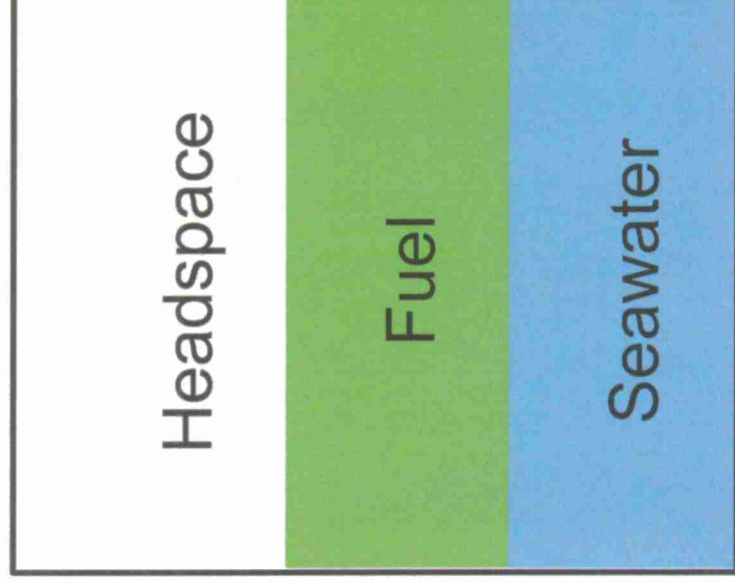
$\text{N}_2$  10%  $\text{H}_2$  0.1%  $\text{CO}_2$

Atmosphere

Air

+ $\text{O}_2$

+ $\text{O}_2$



**OU**

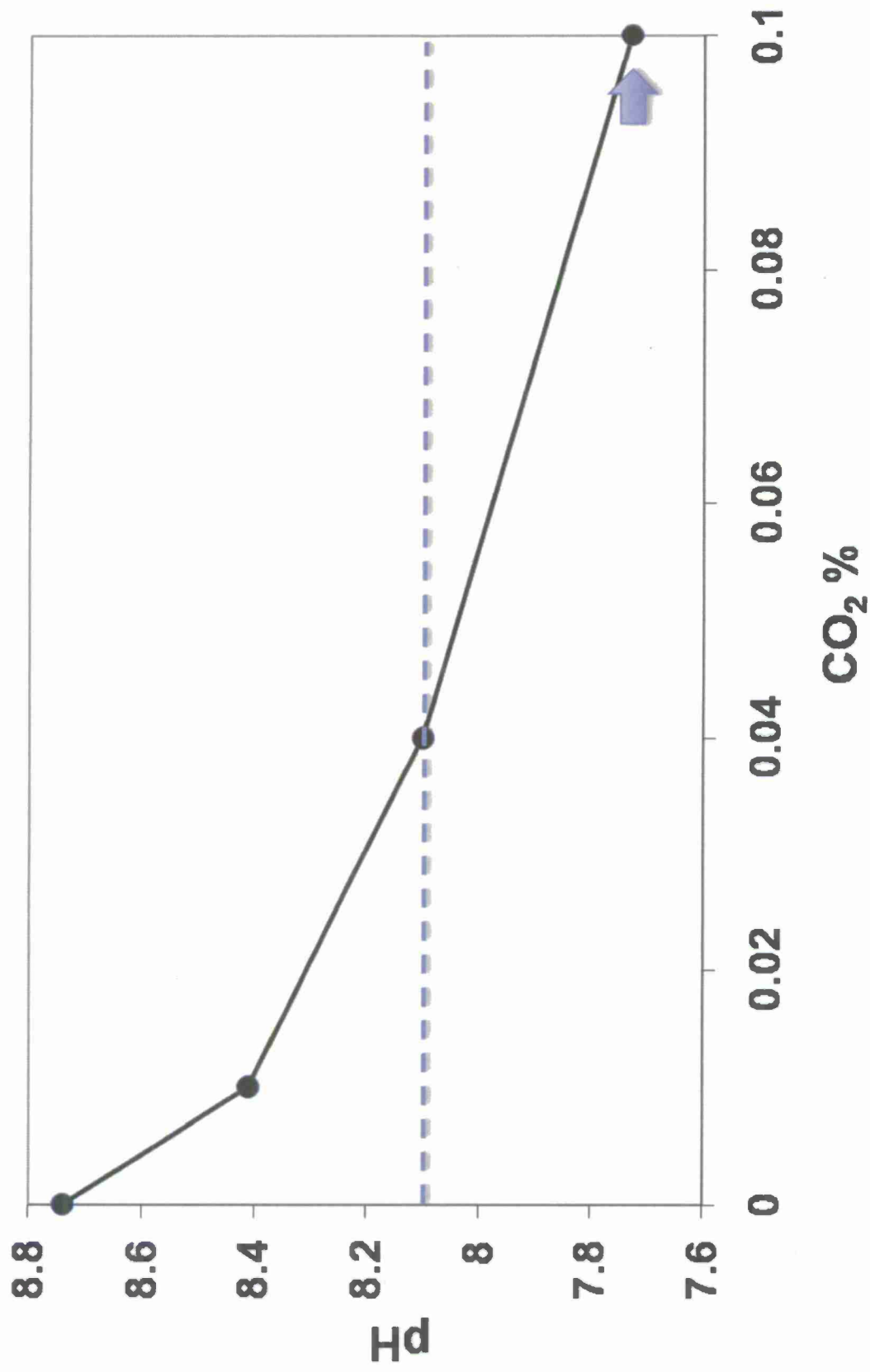
$\text{N}_2/\text{CO}_2$  8:2  
Bubbled

No  $\text{O}_2$

No  $\text{O}_2$

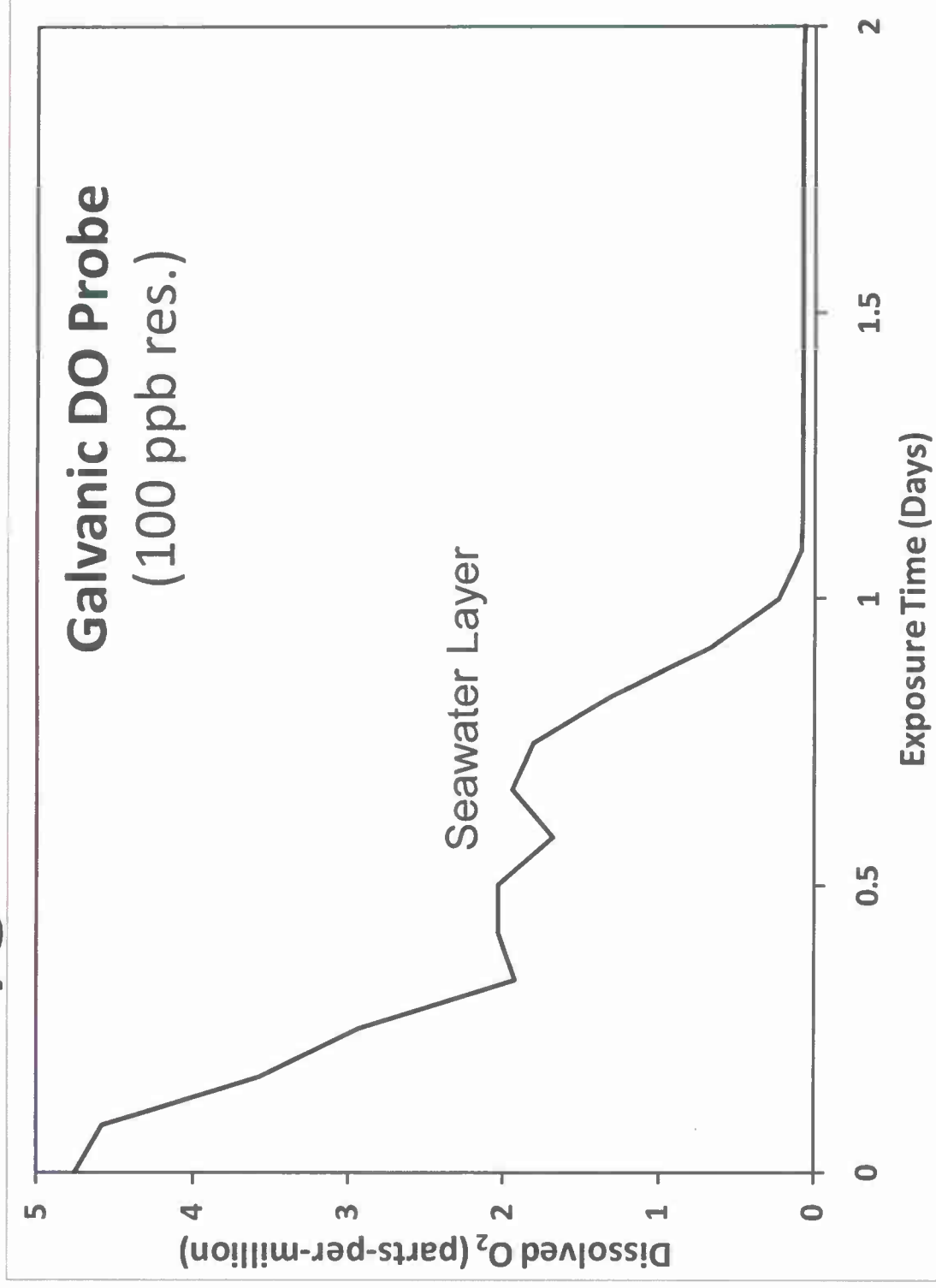
No  $\text{O}_2$





Key West seawater pH as a function of CO<sub>2</sub> % in bubbled mixed gas containing 10% H<sub>2</sub> and balance N<sub>2</sub>.

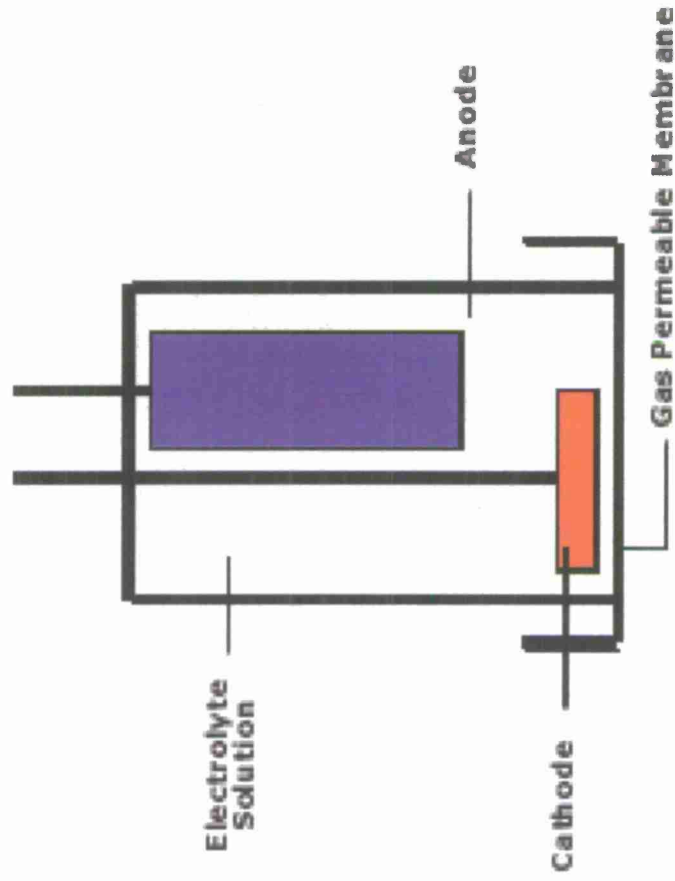
# Oxygen Concentration



# Oxygen Probes

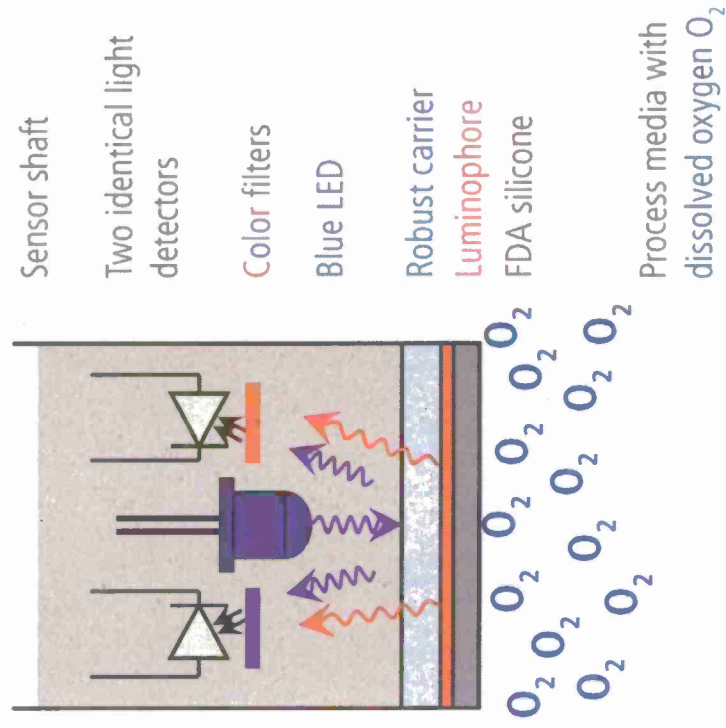
## Galvanic

(100 ppb res.)

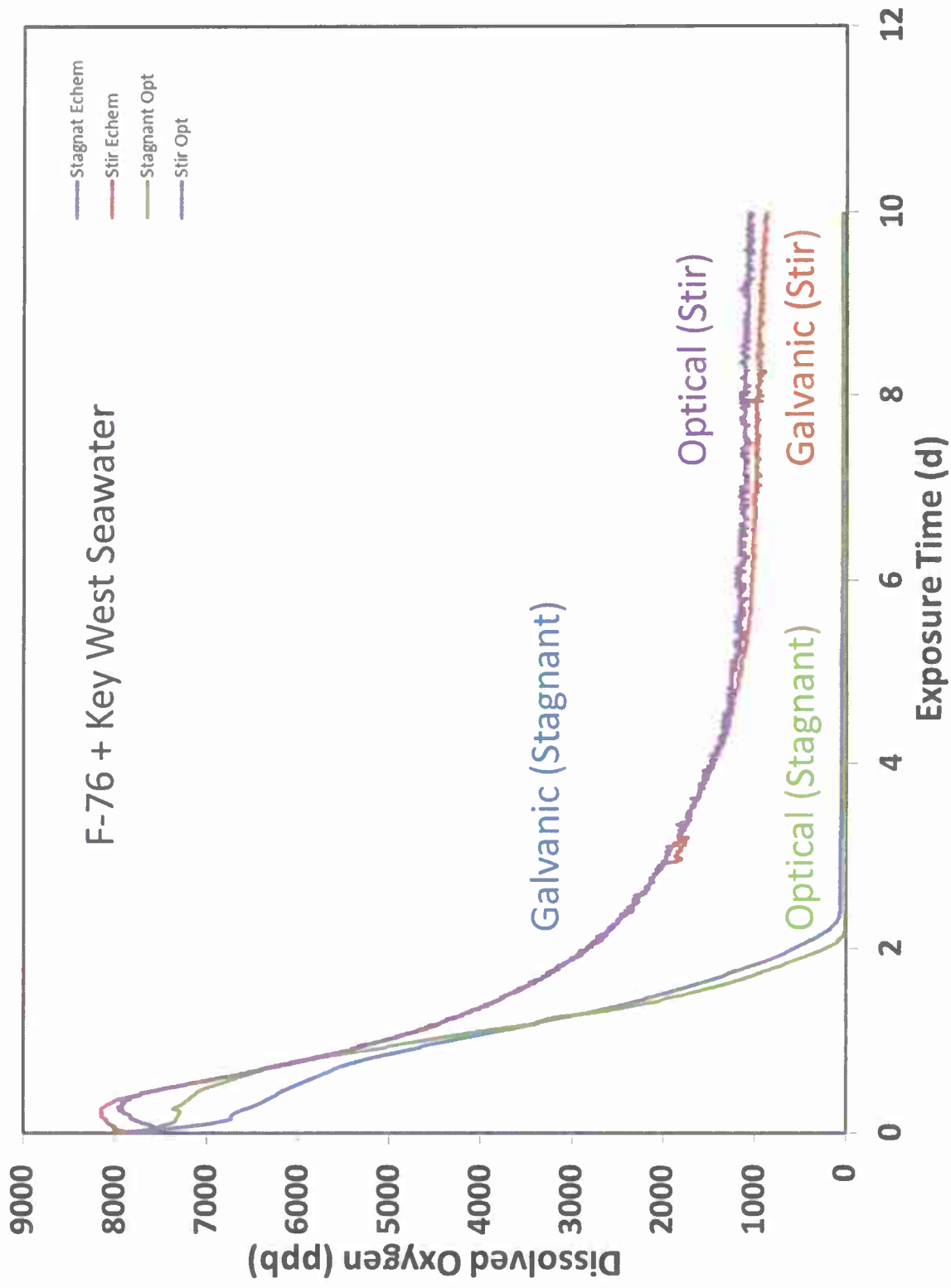


## Optical

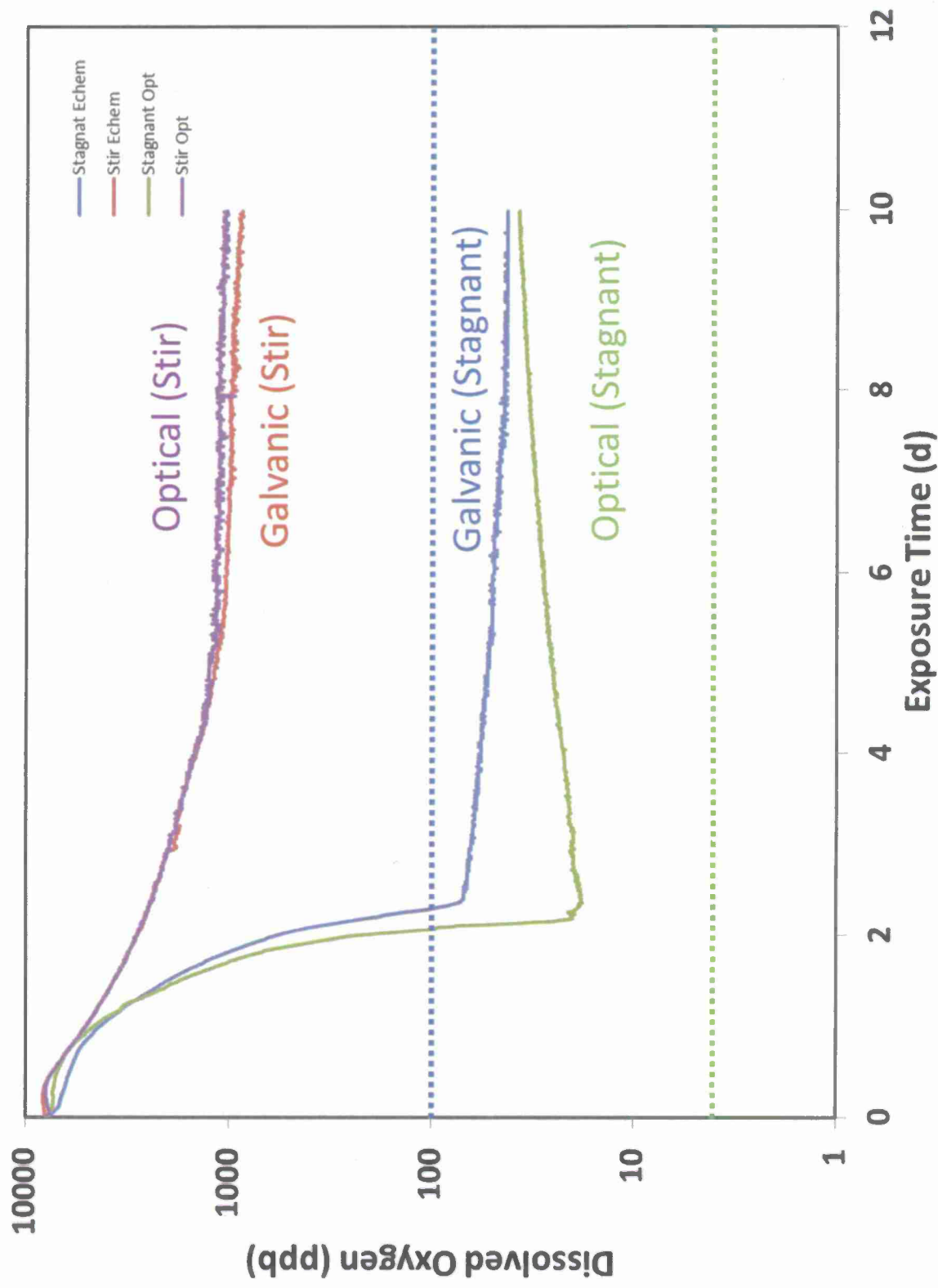
(4 ppb res.)



# Dissolved Oxygen Measurements



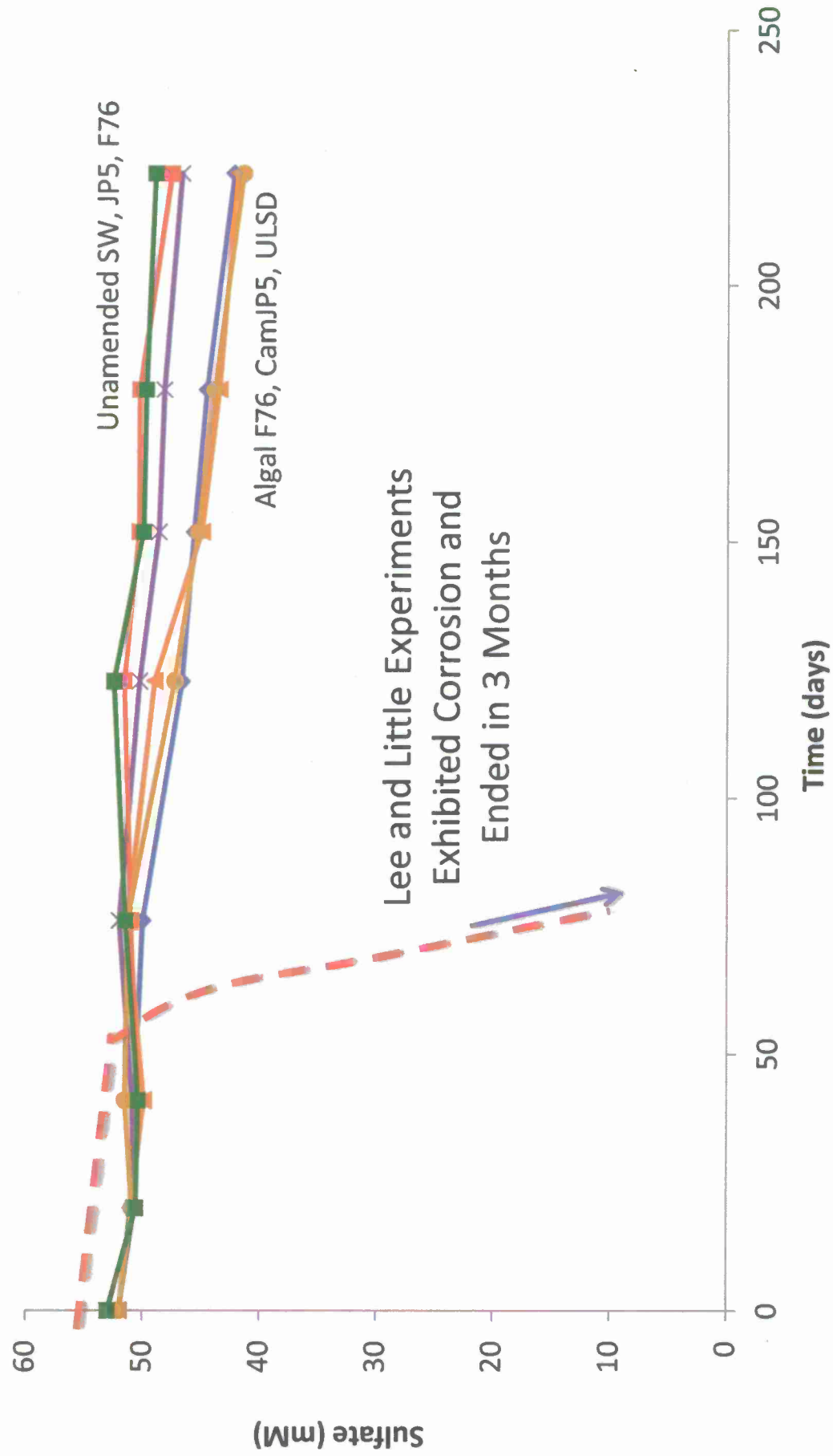
# Dissolved Oxygen Measurements



# Biocorrosion - ULSD and biofuel blends



## Anaerobic Fuel/Seawater Incubations

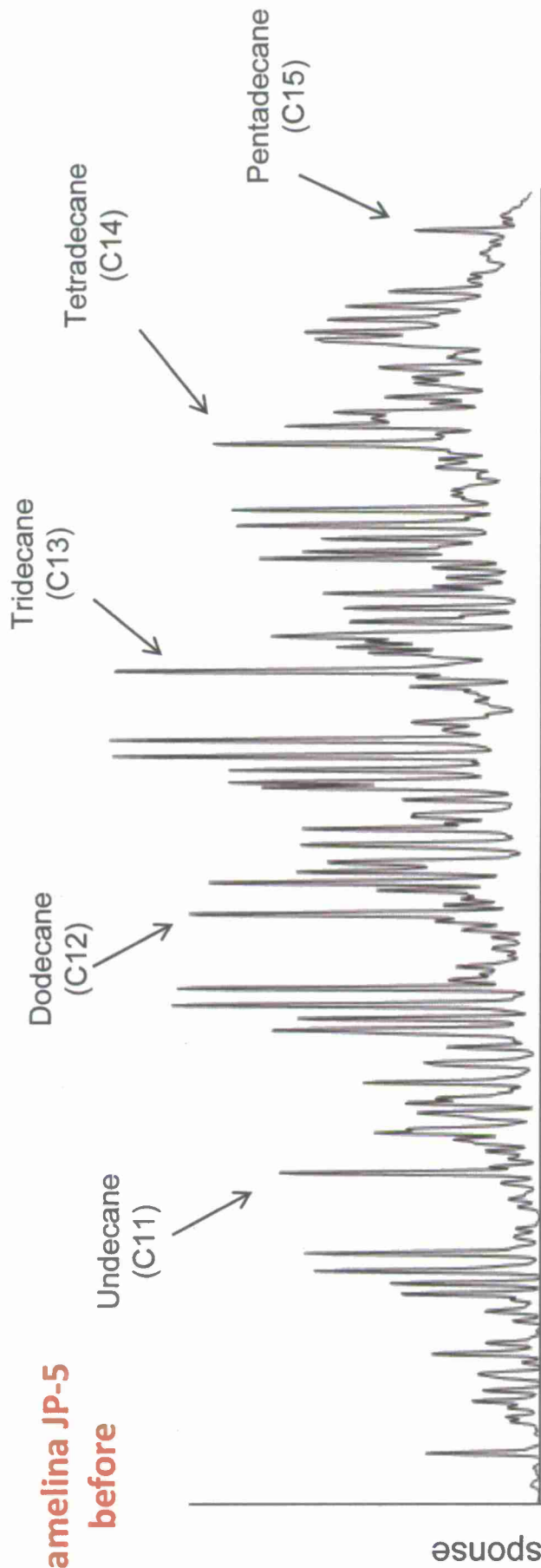


# Biocorrosion - ULSD and biofuel blends

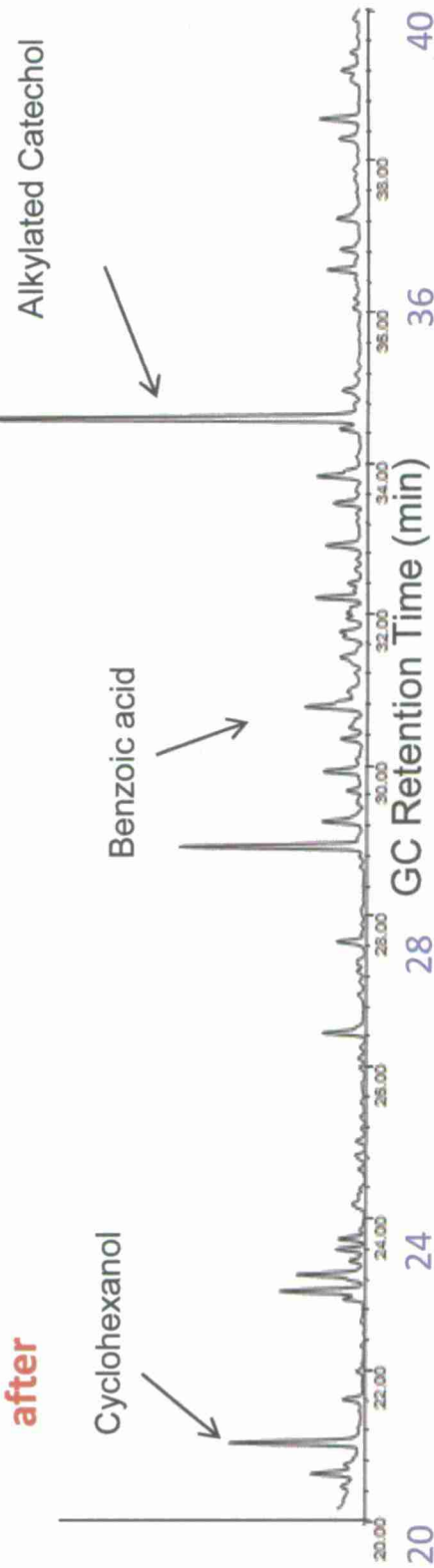


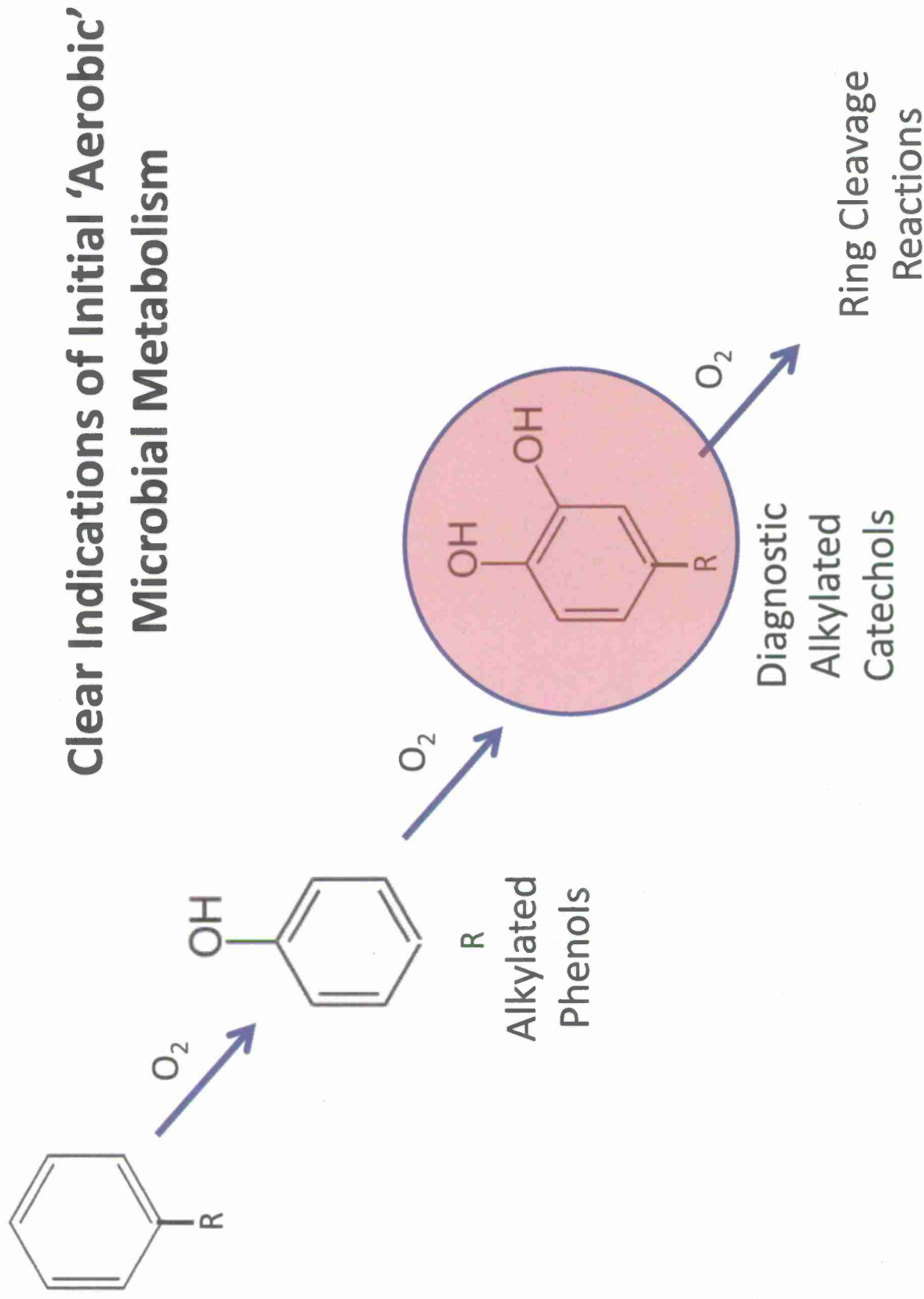
## Metabolite Profile of Fuel/Seawater Incubations

Camelina JP-5  
before



Camelina JP-5  
after

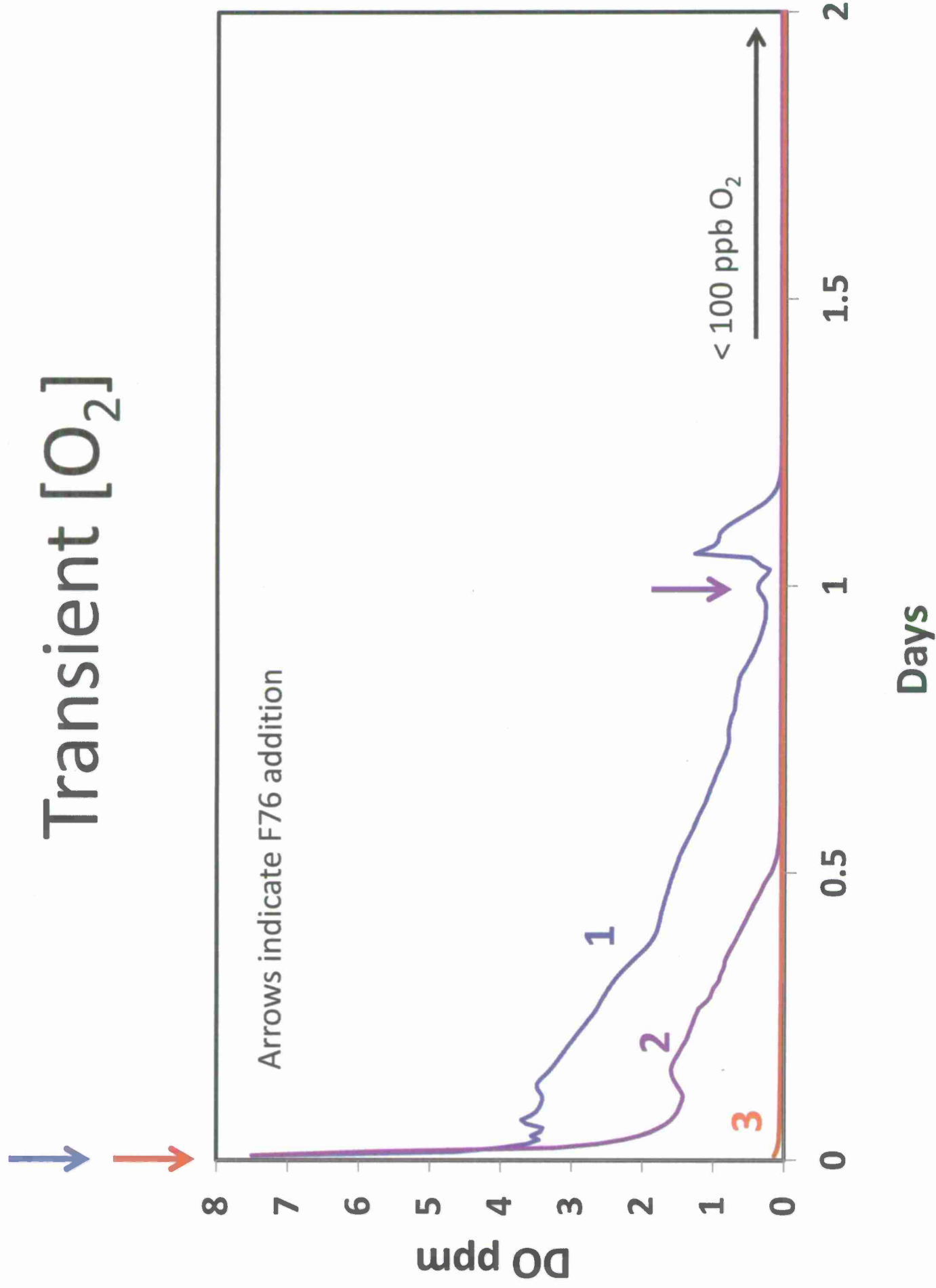




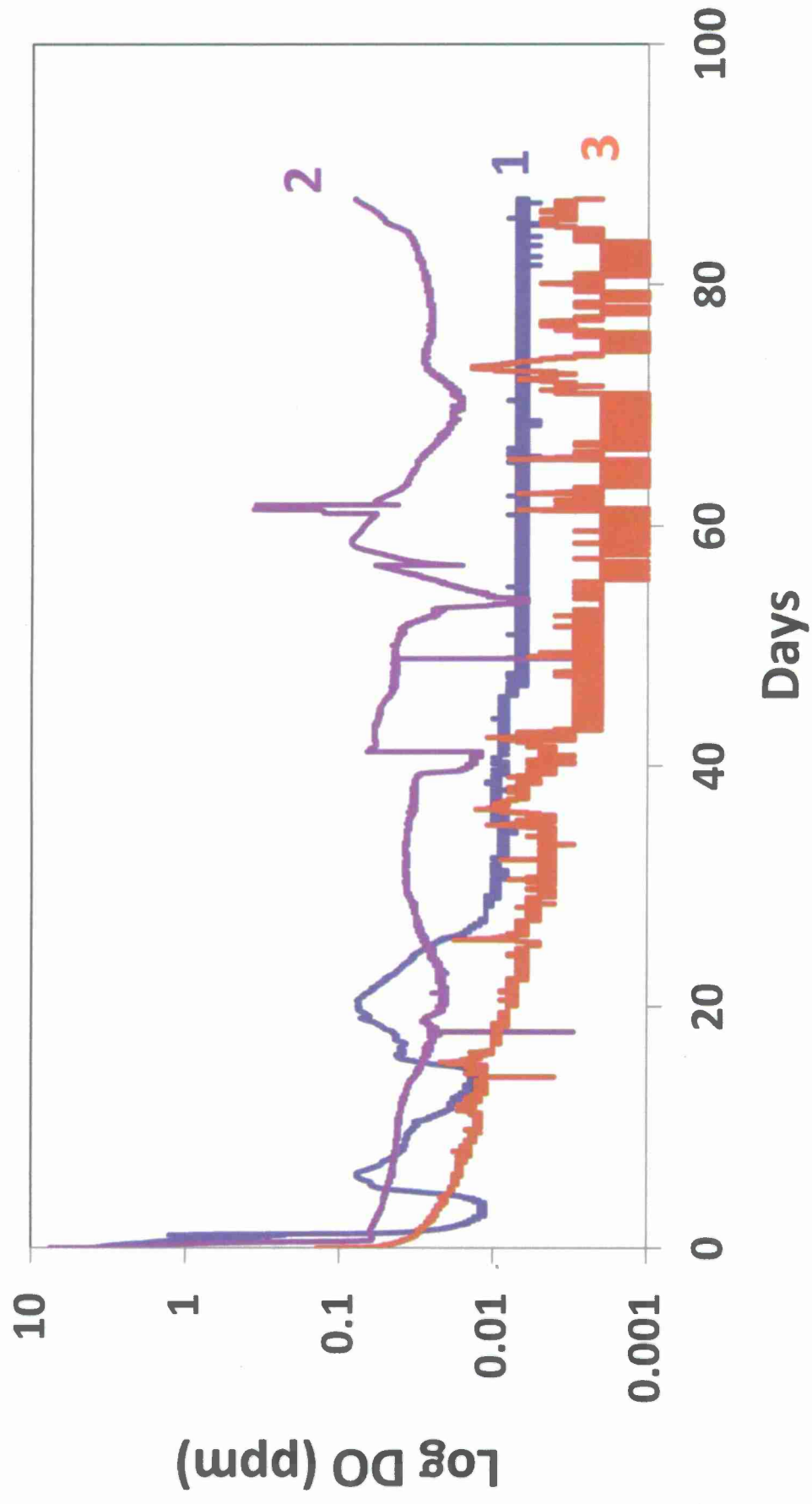
# Experimental Conditions

Case	1	2	3
Gas Mixture	0.1% CO <sub>2</sub> , 10% H <sub>2</sub> , bal N <sub>2</sub>	0.1% CO <sub>2</sub> , 10% H <sub>2</sub> , bal N <sub>2</sub>	20% CO <sub>2</sub> , 80% N <sub>2</sub>
Na <sub>2</sub> S Addition	No	No	150 ppm
Seawater [O <sub>2</sub> ] at Fuel Addition	8 ppm	< 0.1 ppm	0 ppm
Fuel [O <sub>2</sub> ]	~ 60 ppm	~ 60 ppm	0 ppm

# Transient [O<sub>2</sub>]



# Log DO



# Corrosion Rates

